

# A Geoscience Approach to Rock-Solid Concrete

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Concrete, a composite of sand and gravel bound by hydrated cement, is one of the most used construction materials, worldwide. Concrete is used so extensively because it is easy to produce, has high compressive strength, and is durable, which makes it economical in the long term. The quality of durability can be significantly compromised by a number of physical and chemical processes, leading to premature degradation of a concrete structure. When concrete degrades prematurely, the cost of a structure will increase dramatically, and the degraded concrete can pose safety and environmental risks as well. Hence, increasing the durability of concrete is a critical concern in applications ranging from the transportation infrastructure to the isolation of hazardous and radioactive waste and as it turns out, improving the durability of cement-based composites will help with the atmospheric carbon-dioxide (CO<sub>2</sub>) problem.

An important, though indirect, consequence of premature concrete degradation is the unnecessary emission of CO<sub>2</sub>. Cement production is the largest industrial source of atmospheric CO<sub>2</sub> that is not associated with energy production. Figure 1, a photo of a cement plant in Tijeras, New Mexico, shows the stacks from which the CO<sub>2</sub> is emitted into the atmosphere.

Despite the long history of the use of concrete, a mechanistic approach (that is, understanding the entire cement/aggregate system) to control durability has remained elusive. Instead, a prescriptive approach has been used; prescriptions (specifications) have been based on a combination of field experience and laboratory experiments, both of which are limited with respect to duration, properties of the materials, environmental factors, and other variables that affect durability.

In contrast, a mechanistic approach to designing cement-based composites would rely on predicting the physical and chemical evolution of a concrete mix placed in a particular environment. Such an approach has often been viewed as unachievable, given the chemical and structural complexity of a cement-based composite. However, the two primary barriers to this goal (computational and theoretical) are not insurmountable. Recent advances in computa-

tional power and methods (e.g., dual-continuum codes for modeling reactive transport in matrix and fractures) have removed these barriers to predicting the evolution of a concrete structure as it interacts with its environment. The theoretical barrier can be lowered by borrowing tools and approaches used in the geosciences, where they have addressed similar complexities in a mechanistic way.

For example, in many respects, the chemical and physical evolution of a cement-based composite resembles what occurs in natural environments. Most of the materials in a composite like concrete are either earth materials or derived from earth materials. Likewise, the processes that occur during cement hydration or that occur as the composite interacts with its environment can also be directly related to geological analogs. Hence, the methods used to describe geological materials and processes at a fundamental level may prove useful in laying the foundation for a mechanistic approach to concrete evolution.

This concept is the basis for our initiative to develop a geochemical model of the evolution of cement-based composites. The model would allow the prediction of how a concrete mix performs in a particular environment. In other words, one could optimize a mix design prior to

placement. En route to this model, we have been developing a number of geochemical and geophysical methods for characterizing cement-based composites. One of our methods, ASR Detect™, recently received an R&D 100 Award.

## Alkali-Silica Reaction

One of the leading causes of premature degradation in concrete worldwide is the alkali-silica reaction (ASR) between alkali cations, hydroxide anions, and siliceous aggregates. In this reaction, silica dissolves in the high-pH pore fluids and precipitates as a gel along fractures, in voids, and around reactive aggregates in the concrete. Although this phenomenon has been recognized in degrading concrete for over 60 years, ASR remains poorly understood, and the problems it causes have been handled primarily using prescriptions that have been known for decades, which are to minimize the alkali content of the cement and avoid reactive aggregates. These prescriptions are not always successful, and ASR-plagued concrete continues to be produced today (Figure 2). Furthermore, low alkali levels in cement are difficult to achieve in some regions, particularly in light of new regulations that have led to the re-incorporation of alkali-

rich dusts trapped from the exit gases of a kiln. In addition, nonreactive aggregates are not always locally available, and this deficiency will become more of a problem as quality aggregates become depleted.

Several recent treatments offer promise for inhibiting ASR in new structures and even slowing the progression of ASR in existing structures. For example, lithium salts used as admixtures at appropriate levels in a concrete mix appear to inhibit ASR, and soaking a structure with an aqueous solution of lithium may arrest degradation.

### The Geochemistry of ASR

In the field, ASR is conspicuous because it causes a network of surface fractures that are often filled with a white precipitate. The interior of a structure suffering from extensive ASR is also riddled with fractures, along which white precipitate can be seen associated with some aggregates and filling some voids. Unfortunately, these characteristics are not unique to ASR, so a diagnosis typically requires a time-consuming petrographic analysis (for example, verifying the presence of an isotropic gel). Ideally, one would like to diagnose ASR in the field, which would allow the causes of degradation to be determined more rapidly and would allow a better evaluation of the distribution of ASR within a structure at a hand-sample scale.

We recently developed a geochemical staining method for detecting ASR gel in a hand sample. Our method, ASR Detect™, makes use of the physical and chemical properties of the primary reaction product (an alkali-rich gel). The staining method is designed to tag regions containing exchangeable potassium.

Gel produced by ASR is typically enriched in both sodium and potassium, which are believed to originate largely from the cement. Most



**Figure 1. Industrial Source of CO<sub>2</sub>.**

Cement kilns are the largest nonenergy source for anthropogenic CO<sub>2</sub> emissions, producing about a ton of CO<sub>2</sub> for each ton of cement clinker.



**Figure 2. An ASR Problem.**

The underside of an ASR-plagued bridge on I-25 in New Mexico. The 35- to 40-year-old bridge was made using low-alkali cement, yet ASR appeared rapidly in the bridge deck, which has since undergone expensive resurfacing operations.

cements have potassium as their dominant alkali contaminant so ASR gels often have more potassium than sodium. In our observations of ASR gels (primarily in samples from New Mexico), potassium is always the dominant alkali cation. This exchangeable potassium can be used as

a marker for ASR gel by staining with a saturated solution of sodium cobaltinitrite. When such a solution contacts ASR gel, exchangeable potassium from the gel reacts with the solution to form a yellow precipitate  $[K_2NaCo(NO_2)_6 \cdot 6H_2O]$ . This method has also been used in the

geological sciences for staining potassium feldspars that have been etched in hydrofluoric acid. For ASR gel, sodium cobaltinitrite solution is allowed to react directly with the concrete surface without any acid-etching step.

In addition to providing a means for rapid ASR identification in the field, using ASR Detect™ has enabled new insights into the geochemical development of ASR. As can be seen in the stained samples, ASR exhibits a characteristic progression from the initial formation of a potassium-rich gel located within some aggregates and voids to a latter migration and ion exchange to form gels with lower K/Ca ratios that have a more widespread distribution.

This chemical heterogeneity can be seen at a micrometer scale using scanning electron microscopy, and the staining allows the process to be followed at the hand-sample scale.

The heterogeneity of ASR is likely tied to the innate spatial variability of concrete. Heterogeneous microenvironments develop along fractures in a concrete due to the chemical differences between the hydrating Ca-Si paste (pH > 12.5) and the aggregates (often siliceous aggregates that can buffer the local pH at significantly lower values).

We are using this concept of microenvironments as the basis for our geochemical model for ASR.

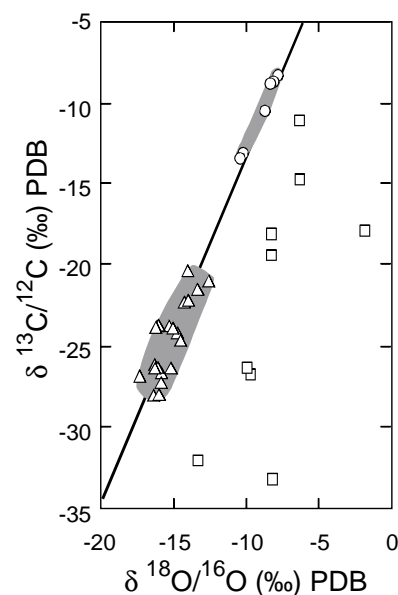
## The Biogeochemistry of ASR

The unique geochemistry of the concrete microenvironments we identified led us to consider whether microbial activity may play a role in ASR. Traditionally, ASR has been viewed as an inorganic process involving the enhanced dissolution of metastable silica (for example, opal, silica glass, and strained quartz) in a high-pH, alkali-rich solution. Hence, the aggregates around which gel was

found were termed “reactive aggregates” and viewed as sources of the silica gel. In our model, these aggregates function as geochemical microenvironments in which the pH may be lowered by acidic mineral surfaces and by mineral dissolution, causing the silica to precipitate. One consequence of this view is that these microenvironments might provide suitable environments for microbial activity, which often is not optimized at the higher pH of the cement paste. We have investigated this hypothesis with a combination of stable isotopic analysis and biogeochemical staining.

Figure 3 shows values for  $\delta^{13}\text{C}/^{12}\text{C}$  and  $\delta^{18}\text{O}/^{16}\text{O}$  from a variety of locations within a degrading concrete system. Shown in triangles and circles are the values measured from two materials actively precipitating at the bottom of a concrete bridge deck (calcite stalactites and thermonatrite efflorescence, respectively). The isotopic ratios in these materials show a marked depletion along a trend with a slope of ~2. This trend results from a kinetic fractionation caused by the high pH of the precipitating fluids. In contrast to precipitation in caves (in which degassing causes stalactite growth), precipitation of the calcite and thermonatrite results from diffusion of atmospheric  $\text{CO}_2$  into the high-pH fluids. These materials define the “inorganic” isotopic trend in this system. The squares in the graph show the ratios measured for samples of gel along fractures within the bridge deck. These isotopic ratios cannot be explained by the inorganic kinetic trend, because their carbon signature is even more depleted. This depletion is believed to reflect an additional (highly depleted) source of  $\text{CO}_2$  caused by microbial degradation of organics.

We confirmed this hypothesis by combining geochemical staining (to show the distribution of ASR gel) with a biological staining method (to show the distribution of protein). An

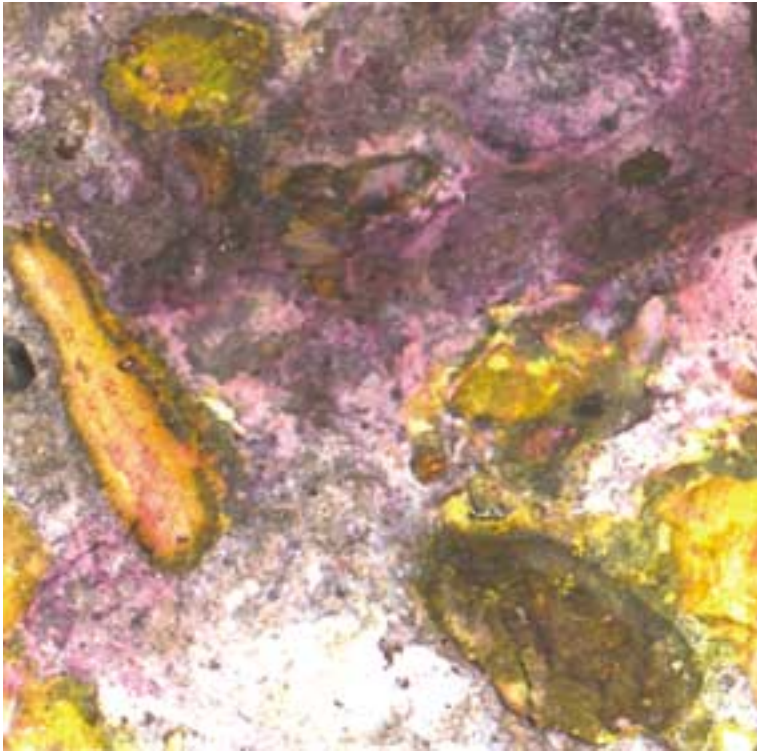


**Figure 3. Isotopic Data.**

The graph shows carbon and oxygen isotopic data from carbonates precipitated in the degrading concrete system.

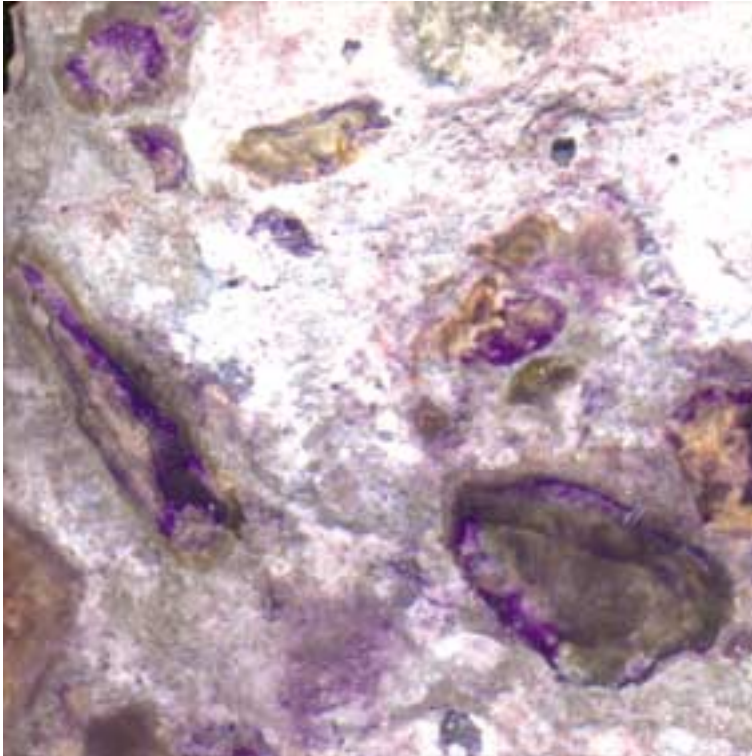
example of this staining can be seen in Figures 4a and 4b. Ninhydrin is often used in microbiology to determine the presence of protein, which results in a purple stain. When stained with ninhydrin and ASR Detect™ (on opposite sides of a fracture), concrete from the structure studied isotopically shows protein accumulation in regions where K-rich ASR gel occurs. This protein accumulation is apparently due to a biofilm in these regions, as determined by scanning electron microscopy.

Given the association of microbial activity with ASR, one might wonder, “What role do microbes play in concrete degradation?” Microbial-induced degradation of concrete has been observed in concrete exposed to sewage. However, the type of degradation that we have observed appears to be quite distinct, with microbial activity restricted to specific microenvironments within the concrete. We plan to elucidate the role of microbes in ASR and to incorporate this role into a predictive model of concrete durability. ■



**Figure 4a. ASR Detection.**

Concrete fracture surface stained with ASR Detect to show characteristic yellow precipitate on ASR gel.



**Figure 4b. Protein Detection.**

The opposing concrete fracture surface stained with ninhydrin to show localization of protein. Note protein (dark purple) is localized in regions of ASR gel.

## Further Reading

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